Manufacturing Macroporous Monoliths of Microporous Metal Organic Frameworks (MOFs)

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ABSTRACT: We report the first use of a pressure-assisted sintering technique on metal-organic framework (MOF) powders allowing for fast production of crystalline macro-porous monoliths. Mechanical and micro-structural characterization of the monoliths is presented. The interconnected macro-porosity of the compacts can be adjusted providing an immense interface

for gas-solid interaction. The sintering technique is well-established and commercially available, allowing industrial scale-up of the process.

The crystalline structures of metal-organic frameworks (MOFs) have been chemically tailored and optimized for an extremely wide range of application[1]. Their selective chemical affinities, combined with large surface area and porosity give rise to microcrystalline powders with sorption functionalities which have been heralded for their potential in large-scale industrial separation processes[2-3]. These fine powders are difficult to handle in industrial settings, such as pressure-, temperature-, or vacuum swing adsorption systems. Powders can clog reactors and pipes, cause pressure drops in columns due to compaction, and have inherent drawbacks of low volumetric performance. A lack of suitable processes for converting functional MOF powders into usable forms is a significant limit on the deployment of this technology[4]. In particular, their 'soft' nature leads to structural collapse or architectural destruction upon application of pressure in industrial applications[5].

Physical engineering processes, still in their nascent stage with MOFs, have produced membranes and films as the most common morphologies, and this allows for continuous molecular filtration[6]. Packed-bed systems on the other hand are envisaged for adsorption-based separation, particularly for gas capture and storage.

There are very few reports on attempts to manufacture monolithic MOF structures for gas sorption. Mechanical densification of MOF-177 resulted in bulk densities up to three times higher than crystallographic densities[7], which was associated with reduced micro-pore volume due to progressive pressure-induced amorphisation[8]. Extrusion processing of HKUST-1[9] and MIL-101(Cr)[10] achieved monolithic structures with unimpaired crystallinity, but with the aid of polymeric binders. The latter however can block pore volume and coat surface area, with

deleterious effects on adsorption capacity[11]. Hot-pressing assisted crystal-growth onto substrates has been explored for a range of MOF structures[12]. This method, while avoiding the use of binders, is limited to producing thin layers and coatings. Slow drying of ZIF-8 precipitates in molds did, however, yield three-dimensional monolithic structures with good mechanical properties, high bulk densities, and unimpaired porosity[13].

Direct sintering of pure MOF powders as a consolidation process is, to our knowledge, unexplored in the field of MOF engineering. The advantages of sintering in conventional applications include the end result of shaped products with tuneable porosity. Two steps are required in the simplest form of this direct method: (1) formation of a "green" body by pressing powder into a mold and (2) heat treatment to fuse the particles together. In contrast, pressure-assisted sintering (for example, hot pressing) combines these two steps in one. Moreover, pressure-assistance has been shown to lower the required sintering temperatures of certain ceramics and metals[14].

In the present study, we exploit pressure-assisted sintering specifically using the Field Assisted Sintering Technique (FAST) method. In FAST sintering, also referred to as SPS (Spark Plasma Sintering), machine rams compress the sample uniaxially. Simultaneously, the rams act as electrodes passing a pulsed direct current through punches and die made of high strength graphite (Figure 1), generating resistive heat. Depending on the electrical conductivity of the material to be sintered, heat is also generated internally in the contained powder compact. Industrial dimensioned machines allow for large net shape to near-net shape production[15].

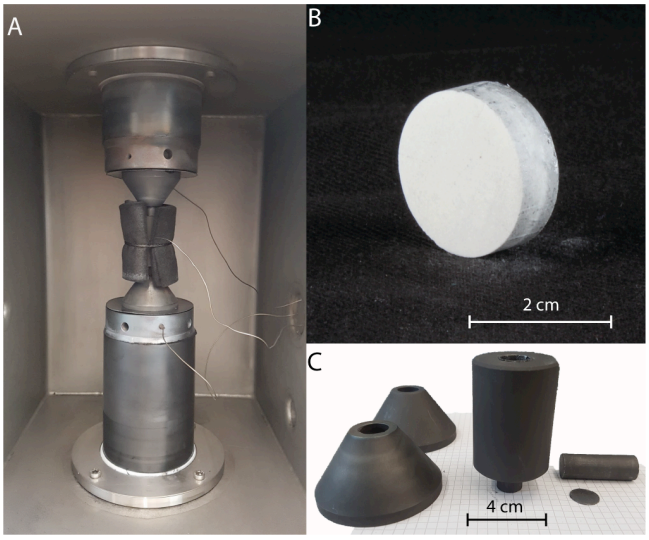

Figure 1. A: Process chamber of FAST sintering facility. B: photograph of sintered crystalline ZIF-4 monolith. C: Graphite pressing tools.

As a model MOF compound, we focus on the zeolitic imidazolate framework ZIF-4 ($Zn(Im)_2$), (Im = imidazolate, $C_3H_3N_2^-$)[16]. This prototypical ZIF compound has demonstrated selectivity of paraffin over olefin[17] and can be produced economically in relatively large quantities[18]. ZIF-4 transforms into the X-ray amorphous *a*-ZIF at approximately 300 °C and recrystallizes into the dense ZIF-zni upon further heating to 350 °C[19]. These processes are kinetically-controlled and take effect over a range of temperatures and dependent on heating rates and temperature-time profiles.

Monoliths of all three polymorphic phases have been manufactured by controlling sintering conditions as set out in Table 1. Experimental details of synthesis, sintering, phase identification, and characterization can be found in the Supporting Information. Sample **A** consists of pure, crystalline, ZIF-4. Interconnected macro-porosity amounts to 40-45 % of the total volume, as calculated from micro-CT data (Figure 2), and confirmed by comparison of He-pycnometric skeletal density with bulk density. This porosity is the result of a grain supported microstructure and thus controlled by the particle size of the starting powder. Milling or fractionation of the as-

synthesized material or controlled crystal-growth are two mechanisms that can be adopted to achieve specific pore characteristics, for example size, size distribution, and shape. Such microstructural control also allows for adjustment of bulk mechanical properties. Sample **B** consists of amorphous *a*-ZIF. Sample **C** shows a fully recrystallized phase composition of pure ZIF-*zni*. The microstructure of these glass-ceramic-like materials is relatively dense, with only a small fraction of isolated porosity (Figure S3). Figure 3 shows linear thermal expansion from thermo-mechanical analysis (TMA) and mechanical test curves from compressive strength and nanoindentation for monoliths of all three phases. Bulk coefficients of thermal expansion (CTEs) for appropriate temperature ranges are set out in Table 1. These bulk CTEs are isotropic and represent the sum of randomly oriented anisotropic domains. By using TMA we were also able to determine the CTE of amorphous *a*-ZIF. These values are applicable to engineering problems. CTEs based on unit cell dimensions measured by variable temperature powder XRD of crystalline ZIF-4 and ZIF-*zni* can be found in Figure S5 for comparison. Interestingly, CTEs of the crystalline lattice are strongly anisotropic. Both ZIF-4 and ZIF-*zni* show negative thermal expansion in at least one crystallographic direction. In sum however, the resulting volume thermal expansion as measured by XRD is still positive.

Elastic moduli and hardness values are systematically lower compared to reported nano-indentation values[20]. We interpret this as the response of a softer grain support: The individually-probed crystals are embedded in a weaker medium compared to the more ideal setting of epoxy-embedded single crystals. This effect is most pronounced in the porous structure of Sample A. Additionally, uniaxial compression during sintering may have affected the mechanical integrity of the crystallites.

Table 1. Sintering conditions and bulk material properties of sintered ZIF-4 powders.

#	Phase	Temperature /ºC	Pressure /MPa	α* /10^{-6}*K^{-1}	Skeletal density /g*cm^{-1}	Envelope density /g*cm^{-1}
A	ZIF-4	250	10	14.2(1)[a]	1.52(1)	0.84(1)
B	*a*-ZIF	300	50	30.3(1)[b]	-	1.58(1)
C	ZIF-*zni*	430	50	8.5(1)[c], 4.3(1)[d]	-	1.55(1)

*Thermal expansion coefficient α [a] 30-250 ºC, [b] 30-200 ºC, [c] 30-350 ºC, [d] 350-480 ºC

The use of MOFs as solid sorbents for harmful substances presents yet another encouraging opportunity. Of particular interest is the capture of radioactive iodine in nuclear waste reprocessing plants and from contaminated sites. Crystalline ZIF-4 has been shown to successfully adsorb iodine and retard its release at elevated temperatures after mechanical amorphisation[21-22]. Applying this repository method requires dense compacts of iodine loaded, amorphized ZIF rather than loose powder. Such compacts ideally consist of mechanically, thermally and chemically stable phases, especially in view of diverse repository conditions. The success of our sintering experiments on ZIF-4, including the possibility to control amorphisation of the latter, provides proof-of-concept for a novel route to achieve compact, volume efficient material for waste encapsulation.

Recent advances in the study of the production and properties of MOF melt-quenched glasses (MQG) tops the growing list of potential applications of these materials. Single-crystalline ZIF-4 samples have been shown to retain their characteristic connectivity after super-cooling from the liquid state[23]. This transfer of chemical functionality from the crystalline to the solid amorphous state opens up a large area of novel potential applications. It is therefore desirable to extend the process of MQG formation to a bulk level. Given the high viscosity of theses melts, retention of

shape on MQG formation of an initially monolithic structure can be envisaged. On the basis of fully densified, mechanically robust and homogeneous compacts, MQG parts could be manufactured by heat treatment of sintered parts.

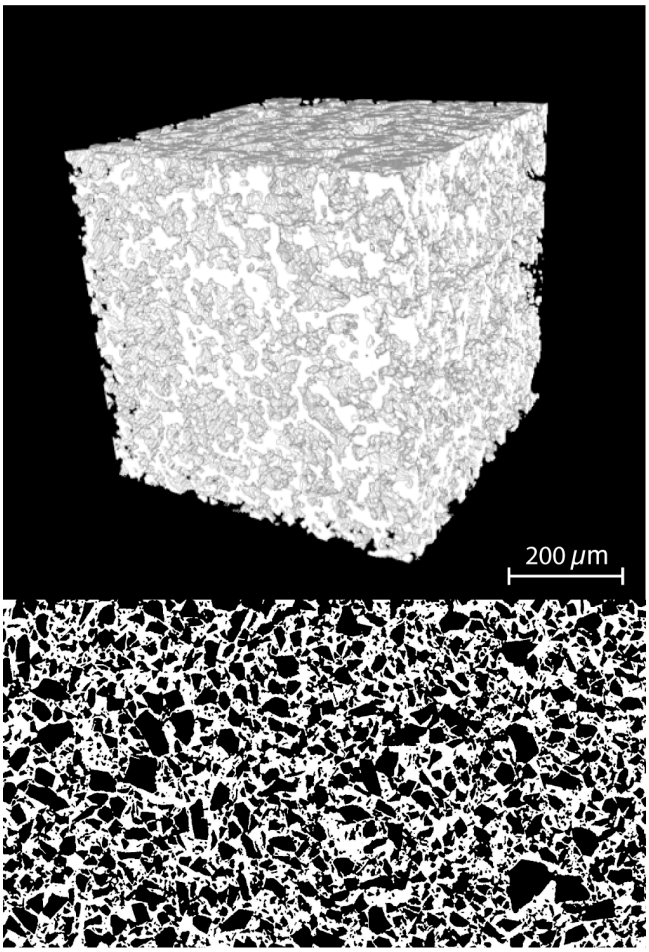

Figure 2. Two- and three-dimensional imaging of a highly porous monolith (sample A, 250 °C, 10 MPa) consisting of pure, crystalline ZIF-4. Top: X-ray micro-tomography. Bottom: Thresholded SEM-BSE image of polished surfaces. White color represents pore space. The scale bar is the same for both images.

In summary, the sintering approach to the design of monolithic MOF structure presented here opens up an industrially-viable, upscalable process. Advantages include near net-shape fabrication and controllable macro-porosity. The thermal and mechanical properties of the

resulting monoliths were assessed and shown to strongly depend on the stabilized phase. Future work needs to be directed towards the control by sintering conditions on mechanical and structural properties of sintered compacts.

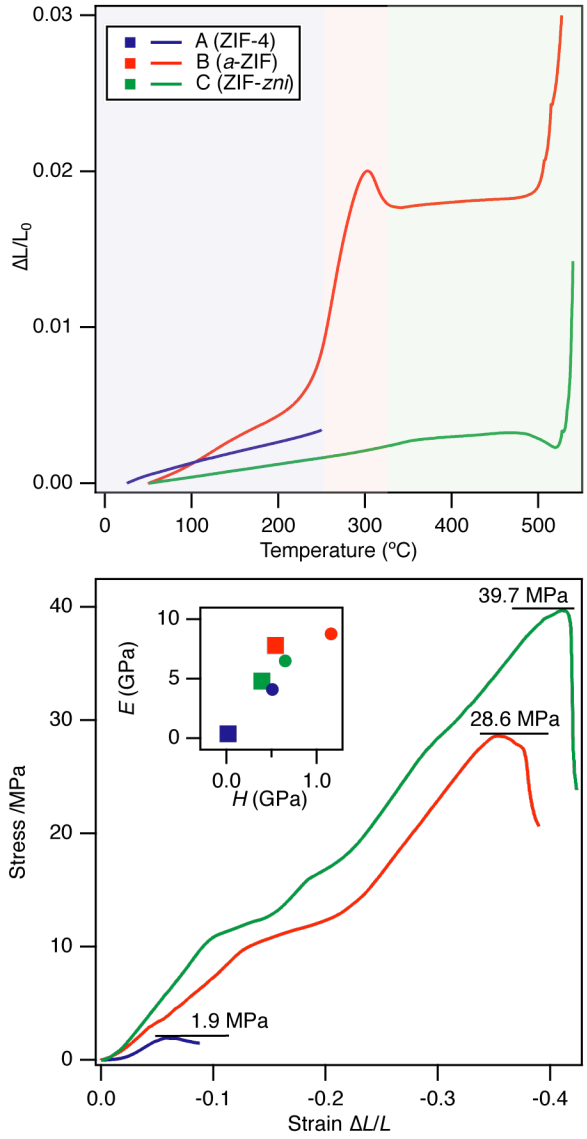

Figure 3. Thermo-mechanical characteristics of sintered monoliths of ZIF-4, *a*-ZIF, and ZIF-*zni*. Top: Linear thermal expansion from TMA. ZIF-4 only shown in its stability region. Recrystallization of *a*-ZIF to ZIF-*zni* results in strong expansion and non-monotonic behavior. Bottom: Stress versus strain plot of compressive testing of monoliths of all three phases. Insert:

Elastic moduli versus hardness values from nano-indentation measurements (squares our data, circles from reference[20], error bars are smaller than the symbols).

ASSOCIATED CONTENT

Supporting Information.

The following files are available as supporting information:

Synthesis procedure and detailed characterization techniques, XRD patterns of all described phases (Figure S1), particle size distribution of starting powder (Figure S2), SEM images of amorphous and recrystallized monoliths (Figure S3), sintering process log files (Figure S4), anisotropic lattice thermal expansion data (Figure S5). (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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